

STUDIES OF WATER-IN-OIL EMULSIONS AND TECHNIQUES TO MEASURE EMULSION TREATING AGENTS

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ABSTRACT

This paper summarizes studies to determine the physics of water-in-oil emulsion formation, the development of procedures to form emulsions, the measurement of emulsion stability and the development of laboratory effectiveness tests for water-in-oil emulsion breakers and inhibitors.

Studies of analytical means for characterizing emulsions show that the measurement of water in emulsion using Karl-Fischer titration is accurate and rapid. This method is limited by the characteristic of emulsions to contain a significant amount of "excess" water. Methods to remove this water have been investigated. These include use of sorbents and centrifugation. Both have limitations that suggest these methods do not have potential for further development.

Viscosity has been found to be a very reliable method of characterizing emulsions. Viscosity measurements are somewhat subject to errors resulting from the incorporation of "excess" water, however, not to the degree of direct water analysis.

Conductivity was investigated as a technique to study emulsions. The findings are that stable emulsions show little difference in conductivity from unstable emulsions.

Emulsion stability was studied using emulsions formed in three apparatuses. For laboratory purposes, an emulsion is generally defined as being stable if it retains most of its water over a 5-day period and shows little reappearance of the starting oil. Based on tests and previous experience in the laboratory, visual criteria have been developed to gauge whether an emulsion is stable or not. These criteria include the characteristic red colour of an emulsion, appearance of water and appearance of "black" oil on the emulsion surface.

Viscosity, water content and appearance were recorded for a series of emulsions over periods of up to 14 days. Most emulsions increased in viscosity over the time period. All stable emulsions also increased in viscosity over the time period and this viscosity increase could be noted in as little as 2 days and very reliably in 5 days. Those emulsions that did not increase in viscosity are suspected to be unstable. Furthermore, these same suspect emulsions had low viscosities in comparison to the stable emulsions. A rule of thumb is that a stable emulsion is one which has a viscosity at least 100 times its starting oil viscosity and this viscosity increases upon sitting over a 5-day period.

Laboratory formation techniques were examined in 4 apparatuses. The most viscous and stable emulsions were produced in the highest energy devices. The most energetic device, a commercial blender, could produce stable emulsions from oils that a rotating flask device could not. A commercial rotary agitator shows promise for a

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standard formation technique at lower energy.

Four tests have been developed to assess commercial emulsion breakers and inhibitor products. The tests mimic open and closed systems and focus on emulsion breaking or inhibition of formation. The open system test incorporates a high oil-to-water ratio to mimic the application of product on the open ocean. The closed system mimics the application of a product to a tank or skimmer where there is not a large amount of water. Two treating agents, Vytac DM and 60% Alcopol 0, were tested in these systems and found to be effective at ratios varying from 1:7000 to 1:250, depending on product and test.

Introduction

Water-in-oil emulsions often called "chocolate mousse" or "mousse" among oil spill workers, are a very important facet of oil spill cleanup. The formation of emulsions changes the properties and characteristics of oil spills to a very large degree. Stable emulsions contain between 50 and 80% water thus expanding the volume of spilled material from 2 to 5 times the original volume. The density of the resulting emulsion can be as great as 1.03 g/mL compared to a starting density as low as 0.80 g/mL. Most significantly, the viscosity of the oil typically changes from a few hundred cSt to about one hundred thousand cSt, an increase of 1000. This changes a liquid product to a heavy, semi-solid material. Emulsification is felt by many to be the second most important behavioral characteristic after evaporation. Emulsification has a very large effect on the behaviour of oil spills at sea. As a result of emulsification, evaporation slows by orders-of-magnitude, spreading slows by similar rates, and the oil rides lower in the water column, showing different drag with respect to the wind. Emulsification also has significant effects on spill countermeasures. Emulsions are hard to recover mechanically, treat or burn.

Previous papers by this group (Fingas et al. 1993a, 1993b; Bobra, 1990, 1991, 1992) focused on reporting on five years of study of several facets of oil emulsions. The group has worked on the development of tests for emulsion breaking chemicals, on the basic physics of emulsion formation, tests of emulsion stability and characterisations of emulsions by measurement of their properties. This series of studies has shown that the topic of emulsions is very difficult and new facets are constantly being revealed. Some of the complexity originates from the many issues involved. Oil consists of hundreds of components and the emulsion consists of water interacting with certain of these components. The formation of emulsions is due to the surfactant-like action of the polar and asphaltene components of oil. These compounds behave like low HLB (Hydrophilic to Lipophilic Balance) surfactants and stabilize water droplets in the oil. The polars and asphaltenes are stabilized in many crude oils by the aromatic solvents, especially the BTEXs (benzene, toluene, ethylbenzene and xylenes). If these compounds are in low quantity or are lost through evaporation, the polars (or resins) and asphaltenes can precipitate (or are no longer solvated) and thus can stabilize the water-in-oil droplets. A relatively large amount of energy is required to form these emulsions once the chemical conditions are correct. This mechanism of emulsion formation has been verified by several experiments including the creation of "artificial" crudes and the doping of crudes. The mechanism is sufficiently well understood that work can now proceed on the prediction of emulsion behaviour of crudes knowing the content of the resins, asphaltenes and the BTEXs (Schramm, 1992).

This paper will report on work done in the past year, focussing on 5 specific

centrifuge, further separation was possible by first overcoming structural barriers and inducing further coalescence. More viscous emulsions were unaffected by the procedure, with the exception of a small layer of water at the bottom of the tube.

A study was performed using 50 ml centrifuge tubes to generate a sufficient amount of sample to analyze. Emulsions were chosen that were formed in lower energy shakers and at least two weeks old, so that they were known to be stable. As well, several different emulsions were used. The samples were centrifuged for one hour, the oil and water removed and weighed, then the emulsion layer was stirred and centrifuged for another hour. At the end of this process, the water content and viscosity were measured to compare with the original values. The results show that the viscosity generally increases with centrifuging, often significantly. The lone exception was a more stable emulsion. Table 1 shows the analytical results from these measurements.

The biggest surprise was the Arabian Light emulsions, that actually increased in water content, while the viscosity jumped over 20 times the initial value, becoming very much more stable. It appears that as the oil and water not associated with the emulsion were removed, a more stable emulsion was left behind. This has implications for the formation and stability of emulsions, as the same compounds responsible of emulsion formation that exist in stable emulsion also are present in the less viscous emulsions, but in lower quantity. In fact, on this occasion, a stable emulsion was left behind when the "black" oil was removed. For the purposes of emulsion analysis, however, the question arises as to whether the centrifuged sample is representative of the original emulsion. Given the dramatic change in properties for the low viscosity emulsions, this method is not suitable for routine analysis.

Water Removal by Centrifuge - Method The centrifuge used is the International Clinical Centrifuge, no model number is specified. Corning 50 mL open mouth centrifuge tubes are filled with approximately 30 g of sample. The centrifuge is run at 2500 RPM which yields a relative centrifugal force of 1100. Samples are centrifuged for one hour. Subsequent analysis is performed by measuring weight, viscosity and water content. The method details are as follows: tare the centrifuge tube, noting the weight for balancing the tubes in the centrifuge. Add approximately 30 g emulsion to the tube. Weigh and adjust to proper range. Balance the tubes and insert into the centrifuge tube holders. Start the centrifuge and spin for one hour. Take out the tube and remove the oil layer using a tared needle and syringe. Calculate the mass of the oil layer. Using a tared needle and syringe, insert the needle below the remaining emulsion to remove the water layer. Wipe off the needle and reweigh to obtain the mass of the water. Reweigh the tube and emulsion, subtracting the weight of the tube. This gives the weight of the remaining emulsion. The mass unaccounted for is assumed to be emulsion lost on the needle during water removal. Gently stir the emulsion with a stirring rod, and repeat the procedure. Carefully balance the tubes, accounted for the reduced mass in the tubes (water can be added to the tube holders to make up any difference). Total the results for the two centrifuge runs and perform water content and viscosity analysis.

Table 1 Treatment of Emulsions with Centrifuge						
Emulsion	% Oil	% Water	% Emulsion	Water	Viscosity @ 15C (cP)	
RA Formed*	Removed	Removed	Retained	Content	D=1 s ⁻¹	D=5 s ⁻¹
Sockeye	0	13	87	84.80	474400	122413
60/600				82.97	382500	103700
Sockeye	1	18	81	88.55	121708	24958
120/1200				85.13	142200	34330
Point	5	29	66	88.60	53950	5634
Arguello				88.10	121800	13950
Light						
80/800						
Arabian	24	58	18	74.85	4493	1935
Light				86.76	95120	18550
120/1200						
Arabian	21	50	29	76.23	3291	1079
Light				83.81	95260	19420
80/800						
*RA formed = the ratio of oil to water at which the emulsion was formed, both values are in mL						
(1) = D = shear rate in reciprocal seconds						

Emulsion Stability

The most important question related to emulsions analysis, is whether or not they are stable. Stability testing has been performed in the past using emulsions formed in the blender and monitoring the water content over a two week period (Fingas et al. 1993a). From those studies, it was found that the water content of mousse does not change significantly with time. However, observation of emulsions formed for other experiments and stored in a cold room indicated that some, if not all, emulsions thicken over time.

To verify the observation of emulsion thickening, emulsions from five oils were formed in the blender, and their viscosity was measured over a two week period. In that time, three of the five increased in viscosity, while the other two remained the same. One of the emulsions even lost water in that time. It can therefore be concluded that not only are these particular emulsions stable, they do not maintain consistent physical properties after formation. The cause of the observed thickening is postulated to be the coagulation of individual particles that "retain their identity, but lose their kinetic independence because the aggregate moves as a single unit" (Schramm, p.7, 1992). As a result, the viscosity rises. These results are shown in Table 2.

A follow-up study was performed on emulsions formed in less energetic mixers to observe the decay of less viscous emulsions. The goal was to determine some means of distinguishing stable emulsions from unstable ones. The two methods chosen for formation were those using a rotary agitator and the Burrell shaker. The procedures for these apparatus are given below. The Burrell method was altered to provide less energy by adding 800 mL of salt water and only shaking for one-half hour. This resulted in an emulsion of lower viscosity. The emulsions formed from the two methods were black in colour, with the exception of the Sockeye and Point Arguello Light, which had a tinge

Table 2 **Stability of Emulsions Formed in A Blender**

Oil	Time	Water Content Weight %	Viscosity		Appearance
			D=1* cP	D=5* cP	
Arabian Light	Initial	75.5	44820	11810	Brown
	6 hours		30180	7213	
	1 day		36230	9882	
	2 days		29410	8578	
	4 days		25070	9891	
	7 days	70.1	30110	11040	
Iranian Heavy	Initial	74.1	160200	29135	Brown
	6 hours		173200	33680	
	3 day		169450	37880	
	8 days		183000	38730	
Sockeye	Initial	70.3	272550	67020	Brown
	6 hours		243600	68670	
	1 day		297850	73870	
	2 days		277050	75680	
	3 days		243200	73380	
	6 days		297100	83760	
	14 days		364100	111450	
Point Arguello Light	Initial	71.6	197500	49650	Brown
	6 hours		183200	51400	
	1 day		225900	57880	
	2 days		208700	56380	
	3 days		193500	53990	
	8 days		206900	68390	
	14 days		278450	83820	
70/30 ASMB/Calif. Blend	Initial	75.9	377400	66830	Brown
	6 hours		316600	66750	
	1 day		343500	70590	
	2 days		292500	58980	
	3 days		364000	69580	
	8 days		280700	63000	
	14 days		357050	72150	
Endicott	Initial	57.3	7425	3288	Dark Brown
	1 day	57.4	9657	3978	
	3 days	58.9	12450	4923	
West Texas Intermediate	Initial	80.7	850	235	Brown
	1 day	35.5	231	83	
	3 days	36.4	4292	2516	
South Louisiana	Initial	50.1	350	97	Yellow Brown
	1 day	33.6	61	47	Brown
	3 days	29.8	2762	1922	Brown

*shear rate in reciprocal seconds

of red coloration. The emulsions were stored in a cold room at 10 degrees Celsius and monitored over a two week period for water content and viscosity. It was expected that the unstable emulsions would decay to oil and water, while the stable emulsions would remain the same. However, in eighty percent of the samples monitored, the viscosity increased, even while the water content was falling. The viscosity rise was often dramatic, rising up to six times the original value, but more normally between 50 and 100%. Meanwhile, the other emulsions maintained a steady viscosity. The results from these experiments are shown in Table 3.

Further studies were performed on oils not expected to form stable emulsions - Endicott, West Texas Intermediate and South Louisiana crudes. The emulsions were formed in the blender to achieve the most stable emulsion possible. As expected, two of the oils only produced emulsions in the 50-60% water content range, while the other was very unstable at 80% water content, although all were very light in colour. The day after formation the 80% emulsion had decayed to only 35%, as had one of the others. Both had lower viscosity values than at the time of formation. The Endicott emulsion at only 55% water content, showed a rise in viscosity similar to the emulsions observed earlier. Three days after formation, the two emulsions that had been decaying, showed a sharp increase in viscosity, up to 20 times their formation values, 40 times the value of two days before. Apparently, the decay process had stopped, and again the emulsions thickened with time. This observation is very similar to the results of a centrifuge test (described above), in which the emulsion lost a great deal of water and oil to reveal a brown emulsion with a viscosity several times higher than the starting emulsion. Unfortunately, there was insufficient sample to monitor the emulsions for the full two weeks.

A round of experiments in a rotary apparatus was conducted to confirm these findings. The energy in this apparatus is believed to be midway between that of the blender and the Burrell wrist-action shaker. The results of all runs are illustrated in Figure 1.

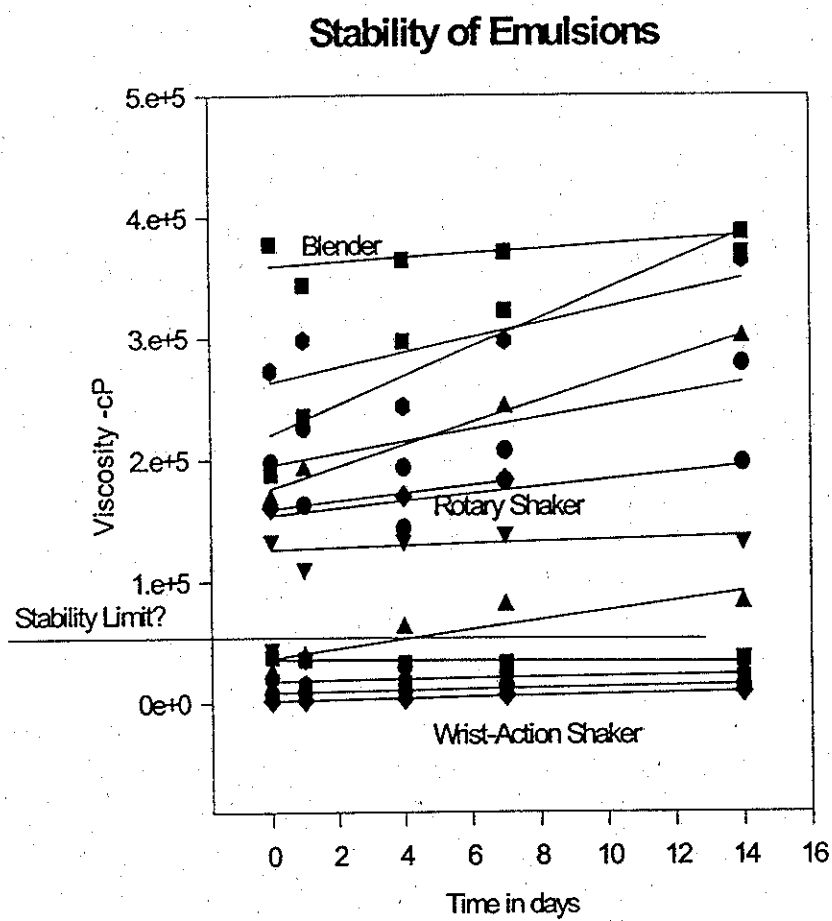
From the above observations and data, a number of conclusions can be drawn. First, an emulsion that does not have the characteristic red appearance might still be stable. However all emulsions appearing above the tentative stability line in Figure 1 have a reddish appearance. Second, emulsions do not maintain constant physical properties with time. Stable emulsions will increase in viscosity with time. Third, an emulsion that loses considerable water may still be a stable emulsion. Fourth, there does not appear to be an easily-definable distinction between stable and unstable. The clear cut distinction above is that any emulsion that increases in viscosity is stable. Those that do not increase in viscosity, may not be stable. The period of time within which a clear trend is evident is between 3 to 7 days. Viscosity alone may not be a predictor of stability, however it appears that unless the emulsion is over 2 orders-of-magnitude greater in viscosity than the starting oil, then it is unstable. Fifth and finally, the three means of creating emulsions result in distinctly different emulsions with distinct viscosity ranges. Energy of formation is then responsible for part of the resulting viscosity.

Table 3 Stability of Emulsions Made in A Wrist-Action Shaker

Oil	Time	Water Content Weight %	Viscosity		Appearance
			D=1* cP	D=5* cP	
Arabian Light	Initial	80.8	7640	2936	Black
	1 day	80.7	8482	3283	
	3 days	80.6	9396	3744	
	7 days	80.9	12840	4687	
	14 days	80.9	13790	5230	
Iranian Heavy	Initial	86.2	37570	8089	Black
	1 day	84.2	35600	10140	
	3 days	83.7	32060	10840	
	7 days	82.8	32000	11080	
	14 days	82.2	35040	12260	
Sockeye	Initial	87.4	134200	26570	Black
	1 day	86.8	111000	23100	
	3 days	85.6	133500	31660	
	7 days	84.3	139100	34890	
	14 days	85.9	133600	29440	
Point Arguello Light	Initial	89.8	24600	4228	Black
	1 day	89.2	38070	6995	
	3 days	87.9	61480	10300	
	7 days	88.8	79340	15520	
	14 days	87.5	81320	16060	
70/30 ASMB/Calif. Blend	Initial	74.9	1509	658	Black
	1 day	72.0	1836	984	
	3 days	72.6	2942	1732	
	7 days	69.9	5658	2524	
	14 days	67.5	8545	4014	

*shear rate in reciprocal seconds

Figure 1



Laboratory Formation Techniques

One of the objectives of the investigation into emulsions is to have a standard method of forming the emulsion from a given oil. The method traditionally used has been the end-over-end rotation of the Mackay apparatus (Mackay and Zagorski, 1982a, 1982b). However this apparatus suffers from not being commercially available. Furthermore, several variations of this apparatus have been constructed, all differently and yielding different results. This apparatus also tends to form emulsions that are not stable, even though a stable emulsion will form from the oil. To compare various means of forming an emulsion and their ability to create emulsions, formation methods for three different apparatuses were developed. Each makes use of a different means of supplying energy to the oil/water system, and are all commercially available.

Rotary Agitator

This apparatus parallels the design of the Mackay apparatus, being an end-over-end rotation of glass cylinders. The apparatus has an advantage in that it is a standard extraction apparatus specified in an EPA standard, unrelated to oil emulsions. The major differences between this and previous rotary apparatuses are the increased height and volume of the bottles and the speed of rotation. The "Mackay" apparatus built in our laboratory has a rotational speed of 65 rpm. The standard motor of the rotary agitator drives the apparatus at 29 rpm. However, a variable speed motor is also available for this apparatus in Canada, capable of up to 56 rpm. A rotation speed of 50 rpm has been chosen for the general method to give a high rotation rate. As well, the increased height of the bottles increases the distance through which the contents fall during rotation. The combination of increased height and higher rotational speed, increases the energy applied. Indeed, higher viscosity emulsions are produced in the rotary agitator than with the Mackay apparatus. The data for emulsions produced in the rotary agitator are shown in Table 4.

When the mixer was first applied for emulsion formation, the conditions of the Mackay test were paralleled as closely as possible. Traditionally the vessel is filled with water to 60% capacity and oil added to the water at a 1:10 ratio. However, the increased volume of the vessels in use required a relative increase in oil volume. In this test, it is desirable to reduce the volume of the oil.

With this in mind, a study was performed to compare emulsion formation on the rotary agitator with the mixing vessels filled to various levels of capacity. The oil-to-water ratio was held constant at 1:10. The results show that lower fill volumes actually improve emulsion formation due to increased energy. The lower limit is dictated by wall effects, in which too much oil adheres to the vessel walls and does not mix properly with the water. A fill volume of 25% of fill capacity was chosen for subsequent tests.

The other way of reducing the oil volume required for a test is by increasing the oil-to-water ratio above 1:10. The first attempts to increase the oil-to-water ratio resulted in failure to produce emulsions, as the higher fill volumes were still being used. The oil had a greater tendency to disperse than to form w/o (water-in-oil) emulsions. To overcome this difficulty, the emulsion was made in two steps. First, a 1:10 water-to-oil ratio was used to generate an emulsion at a low fill volume, then more water was added to increase the ratio. The unstable emulsion originally produced is then lifted off the walls and again agitated. This generally results in a stable emulsion. Several combinations of starting volumes and time of rotation were tried on multiple oils, without any clear indication of a superior method. These data are shown in Table 5.

Table 4 Stability of Emulsions Made In A Rotary Agitator

Oil	Time	Water Content Weight %	Viscosity		Appearance
			D=1* cP	D=5* cP	
Arabian Light	Initial	84.9	19750	5747	Black
	1 day	84.6	14870	4624	
	4 days	82.3	17700	6395	
	7 days	82.1	22860	7956	
	14 days	81.1	22260	8259	
Iranian Heavy	Initial	86.6	38110	8715	Black
	1 day	85.0	74410	20020	
	4 days	83.9	63780	21050	
	7 days	82.7	68640	23300	
	14 days	82.5	67440	24350	
Sockeye	Initial	85.0	160900	42970	Tinge of Red
	1 day	85.6	162700	40100	
	4 days	84.0	143500	37480	
	7 days	82.6	182100	47640	
	14 days	83.9	197100	51690	
Point Arguello Light	Initial	91.1	188000	24880	Tinge of Red
	1 day	90.7	235200	26410	
	4 days	90.5	296700	39090	
	7 days	90.0	322100	56530	
	14 days	91.2	370000	58360	
70/30 ASMB/Calif. Blend	Initial	79.9	167700	49750	Brown
	3 days	80.0	191800	56340	
	8 days	80.8	242100	74990	
	14 days	81.0	299500	85780	

*shear rate in reciprocal seconds

Table 5 **Two-Stage Emulsion Formation**

Oil	Fill Volume (Oil/Water)/Water	Time hours/hours	Viscosity @ 15C (cP)		Water Content Weight %
			D=1 s ⁻¹ * cP	D=5 s ⁻¹ * cP	
Sockeye	(30/300)/300	1/1	84640	21400	84.79
Sockeye	(30/300)/300	2/2	85190	21500	84.7
Sockeye	(30/300)/300	4/4	76430	18390	84.3
Sockeye	(60/600)/450	1/1	70870	18640	84.7
Sockeye	(60/600)/450	2/2	86830	21970	84.7
Sockeye	(60/600)/450	4/4	56680	14600	84.4
Iranian Heavy	(30/300)/300	4/4	7930	4523	76.1
Iranian Heavy	(60/600)/450	2/2	6825	3701	75.0
Iranian Heavy	(60/600)/450	4/4	6119	4156	74.8
70/30 Blend	(60/600)/450	1/1	143150	25400	87.9
Point Arguello Lt	(30/300)/300	1/1	84600	945	89.8
Point Arguello Lt	(60/600)/450	1/1	246950	9000	89.3

* shear rate in reciprocal seconds

Data showing formation of emulsions in the rotary emulsion are presented in Table 6. This line of investigation was terminated when it was found that emulsions could be formed using higher oil-to-water ratios.

Following a study on the Burrell shaker in which the oil-to-water ratio was increased, an oil-to-water ratio of 1:25 was attempted using the lower fill volume on the rotary agitator. This oil-to-water ratio was best on the Burrell and produced a stable emulsion in the rotary agitator. A 1:25 oil-to-water ratio is now used in subsequent experiments, for stability studies and emulsion inhibitor tests.

An observation of note is that emulsions of higher viscosity are formed when the vessels are inserted such that the capped end leads into the direction of rotation. The reason for this seems to be the added turbulence created by the neck region of the bottle as the oil falls, as opposed to falling on the smooth bottom end.

The currently used procedures are summarized in the following paragraphs:

Rotary Agitator - The apparatus is an 8-place Rotary Agitator from Associated Design and is equipped with a variable speed motor from 1.5 to 56 rpm. The mixing vessels are Wheaton 2.2 litre wide mouth glass bottles. The fill is 500 mL salt water (3.3% w/v NaCl) and 20 mL oil. This yields an oil-water-ratio of 1:25. Stability studies are performed at 50 rpm, which is set using a tachometer. The mixture is rotated for 3 hours. The specific method is as follows: place rubber collars on glass bottles at the midway point. Add 500 mL salt water and 20 mL oil to the mixing vessel. Place Teflon lid liners on the bottles and cap. These steps should be performed as quickly as possible to reduce exposure of the oil. Insert the bottles into the rotary agitator at the rubber collars, such that the cap is leading into the direction of rotation. Rotate at 50 rpm for 3 hours. Remove the bottles and pour off the water. Collect the emulsion in an appropriately sized beaker. Analyze for water content and viscosity.

Mackay Apparatus - The Mackay apparatus is home made and the description of one type is in the reference noted above. The device in our laboratory employs 500 mL glass Fleaker jars which are rotated end-over-end at 65 rpm. The fill is 300 mL salt water (3.3% w/v NaCl) and 30 mL oil. This yields an oil-to-water ratio of 1:10. The agitation time is 4 hours. The specific methodology is as follows: measure 300 mL salt water into a Fleaker jar. Using a 30 mL plastic syringe, inject 30 mL of the selected oil onto the surface of the water. Cover opening with plastic wrap and cap with rubber stopper. Place the Fleaker jars onto the Mackay apparatus and clamp down the top. Rotate for four hours. Allow emulsion to settle, then draw off sufficient emulsion for water content and viscosity analysis with a spatula.

Blender

The use of a blender for making emulsions was first used in early emulsion-breaker testing, for creating the most-stable emulsion possible. The method is simple and quick, has the highest energy available, and generates the highest viscosity stable emulsions. The method employed in our laboratory is in the following paragraph.

Blender - The Waring 1 litre Duo Speed Commercial Blender with Eberbach 1 litre borosilicate container with stainless steel blender assembly. The fill is 70 mL salt water (3.3% w/v NaCl), additional 25 mL aliquots as needed and 30 mL oil. The starting oil-to-water ratio is generally 1:4, but variable as noted. The mixture is stirred with 15,500 rpm blade rotation. The mixture is agitated for 30-second intervals until a stable (as determined visually) emulsion forms. The specific methodology is as follows: combine 70 mL salt water with 30 mL of oil in the blender vessel. Turn blender on at low setting for 30 seconds. Stir with a rubber policeman and add 25 mL salt water. Turn on blender again for 30 s. Stop, stir and repeat. If an excess of at least 2 mL water is not present, add another 25 mL aliquot of salt water. Continue to blend, stir and add water until an excess of water is obtained. Additional water is not normally required. When emulsion formation is complete, pour off the excess water and pour/scoop the emulsion into an appropriately sized beaker.

Table 6 Data on Emulsions Formed in the Rotary Agitator

Fill of Capacity Volume % (Oil/Water)	Arabian Light		Iranian Heavy		Point Arguello Light		70/30 ASMB/Calif.		Sockeye	
	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹
30/300 15	86.6	18368	*85.85	7150	87.7	38710	89.3	71270	88.2	72740
60/600 30	*75.8	5779	*82.8	24290	87.2	37840	88.7	55910	88.7	83520
80/800 40	*78.9	4688	*82.5	20320	88.1	53950	87.7	48340	88.2	86815
100/1000 50	*76.0	3291	*82.6	13300	89.8	157900	89.0	44765	88.2	90855
120/1200 60	*74.9	4493	*83.1	14960	88.8	34390	88.8	27745	87.6	77580

* Water loss over 24 hours. 1 - all viscosities are measured at a shear rate of 1 s⁻¹

Wrist-Action Shaker

The Burrell wrist action shaker had been utilized in the past for its emulsion formation ability. It was used specifically to relate the energy of the emulsion breaking test to the energy of formation. At that time, it was found that the Burrell could not always form a stable emulsion. Fill has been found to be an important factor in determining the amount of energy in a vessel. Generally, the smaller the fill volume, the greater the energy. A fill volume of 50% was chosen for continued studies, based on the shape of the mixing vessel. This provides maximum surface area for a horizontal separatory funnel. The result was an ability to produce emulsions of brown coloration, or stable emulsion. Several oils were investigated, varying the oil-to-water ratio to find the optimum value. The emulsion viscosity increases with the oil-to-water ratio. However, similar to the fill volume in the rotary agitator, wall effects limit the upper ratio. The optimum value was found to be about 1:25 oil:water. This ratio is now also in use in the rotary agitator procedure. The results of these tests are shown in Table 7.

As a procedure for forming emulsions, the Burrell Wrist Action shaker does not offer any material advantages over the rotary agitator procedure, with the exception of low viscosity emulsions for study. In consideration of a procedure for testing the tendency of an oil to form an emulsion, the rotary agitator is a better, more controllable method. The detailed method for using the wrist action shaker in this laboratory is as follows:

Wrist-Action Shaker - The specific device used is the Burrell wrist action shaker model 75. This unit is equipped with a top platform mount with large separatory funnel clamps. The vessels used are Nalgene 1 litre Teflon separatory funnels with screw-cap lids. In the study of oil-to-water ratios, 500 mL salt water (3.3% w/v NaCl) was used with varying oil amounts. In the stability studies, 800 mL salt water (3.3% w/v NaCl) is used with 32 mL oil. The latter yields an oil-to-water ratio of 1:25. The oscillation is set at a 5 degree arc at a 20 cm radius. In the oil-to-water ratio studies the agitation time was 2 hours and in the stability studies, 30 minutes. The specific experimental procedures are: measure salt water into the separatory funnel. Add oil using a plastic syringe. Mount the separatory funnels into the funnel clamps on the top platform; be sure all apparatus are at 90 degree angles. Move adjustment arm on the Burrell shaker until an arc of 5 degrees is obtained. Shake for 2 hours. Remove from the shaker and allow emulsion to settle to the top. Drain the water and pour/scoop the emulsion into an appropriately sized beaker. Measure for water content and viscosity.

Overview of Formation Methods

Comparative data on the formation of emulsions in four apparatuses is shown in Table 8. This shows that the most stable and highest-viscosity emulsions are formed in the highest energy device, the blender. The rotary agitator produces the next most stable, the wrist-action shaker follows and finally the Mackay. The recommendation is that either the blender or rotary devices be used to produce emulsions to ensure stability and to ensure inter-laboratory repeatability.

Testing Emulsion Breaking and Inhibitor Agents

Past efforts to develop a single satisfactory test for both breaking and inhibition of emulsions did not yield a highly-repeatable test. The past work pointed out a number of important factors to be considered in examining such tests. A critical factor is the stability of the emulsion being tested. Unstable emulsions will show anomalous results. A second important factor is the type of emulsion breaker being tested. Water-soluble products will apparently change effectiveness as the oil-to-water ratio changes. Some

Table 7 Data on Emulsions Formed in A Wrist-Action Shaker

Ratio Oil to Water	Point Arguello Light		Iranian Heavy		Sockeye		70/30 ASMB/California	
	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹	% Water Content	Viscosity cP ¹
1 to 10	87.0	43003	87.9	20880	87.1	47445	89.2	78150
1 to 15	90.0	57068	86.3	30875	86.1	177650	88.9	89153
1 to 20	90.8	144543	88.2	21313	88.4	247550	74.4	46992
1 to 25	91.9	150505			88.2	149750	72.9	13612
1 to 30	92.5	140000	86.3	28260	87.9	150700		
1 to 40	92.2	151923	86.3	26515	88.4	154400		
1 to 50	92.3	118375	86.5	34043	87.6	153500		
1 to 60			85.3	36505				

1 - All viscosities are measured at the shear rate of 1 s⁻¹

Table 8 Summary of Emulsions Formed in Four Apparatuses

			Blender	Rotary Agitator	Burrell Shaker	Mackay Apparatus
Arabian Light	Water Content	% (w/w)	75.5	84.9	80.8	89.3
	Viscosity	D=1 s ⁻¹	44820	19750	7640	24560
	cP	D=5 s ⁻¹	11810	5747	2936	4754
Iranian Heavy	Water Content	% (w/w)	74.1	86.6	86.2	83.5
	Viscosity	D=1 s ⁻¹	160200	38110	37570	17080
	cP	D=5 s ⁻¹	29135	8715	8089	5950
Point Arguello Light	Water Content	% (w/w)	71.6	91.1	89.8	86.1
	Viscosity	D=1 s ⁻¹	197500	188000	24600	10330
	cP	D=5 s ⁻¹	49650	24880	4228	2775
Sockeye	Water Content	% (w/w)	70.3	85.0	87.4	88.6
	Viscosity	D=1 s ⁻¹	272550	160900	134200	105000
	cP	D=5 s ⁻¹	67020	42970	26570	26480
70/30 Blend ASMB/Calif.	Water Content	% (w/w)	75.9	79.9	74.9	88.2
	Viscosity	D=1 s ⁻¹	377400	167700	1509	56270
	cP	D=5 s ⁻¹	66830	49750	658	13340

*stable emulsions have viscosity >10000 cP

types are somewhat more energy sensitive than others. The third factor is the determination of endpoint. The past studies show that both water content and viscosity are useful as endpoint indicators. Viscosity, however, is more difficult to measure, but is much more precise as an endpoint. The result of emulsion breaking is not usually a water-less oil. "Rag" is produced and the water content of this product ranges between 10 to 40 percent. The large water droplets in this product cause inaccuracies in measurement.

The effects of specific variables are as follows:

1. Stability of the emulsion - Emulsions must be stable to yield consistent and repeatable results, this is easily achieved using a known emulsion-producing oil in a high energy device. Stability can be measured by leaving the emulsions to sit at room temperature. Unstable emulsions will be readily detected by simple observation of coloration within a five-day time period. Emulsions formed at low energy are less stable. Some oils will produce stable emulsions at several water contents providing that high energy is used.
2. Energy in the test vessel - Breaking of the emulsion requires some energy. The energy requirement is variable with different types of agents. The type of energy induction, be it rotation or shaking, does not appear to have an effect. Some emulsion breakers require more energy than others. Some emulsion breakers may not break emulsions when no energy is present.
3. Endpoint test method - A variety of methods were tested but the best appears to be water content by Karl-Fischer titration and viscosity. It has been found that a loss of water as little as 10% can result in the breaking of an emulsion. The presence of large water droplets in a "broken" emulsion makes any water-content methodology noisy. After breaking, all emulsions form "rag" along with black oil. The viscosity of the emulsion is a more consistent method, however it requires a sophisticated viscometer. Interestingly, the appearance of the product may be a reliable indicator. Indications to date, show that a reddish product is a stable emulsion and a black one is generally not.
4. Oil-to-water ratio - The oil-to-water ratio in the test vessel is important to yield a correct result for emulsion-breaking agents. Many agents are water-soluble and when the oil-to-water ratio is large, such as at sea, they are much less effective than those that are not water-soluble. A minimum ratio of 1:300 is required to differentiate these products. A ratio of greater than 1:500 is suggested.
5. Mixing time - Mixing time to yield a final, stable endpoint, is variable with the type of agent. A minimum of one hour has been found necessary to reduce noise. Some tests show no increase in agent effectiveness after three hours. Mixing times up to eight hours were assessed in studies up to 1993. It should be noted that currently mixing times up to 48 hours were assessed and the current testing program includes one test with a 24 mixing time.
6. Settling time/post-treatment - After the emulsion is broken, "rag" remains. This material usually contains large unincorporated water droplets. These must be removed before testing for either water content or by viscosity. Settling of about 15 minutes or more is marginally effective. Centrifuge treatment has been attempted. More work on separation techniques is required since the presence of the water droplets is felt to be responsible for most of the variation in results.

The studies were continued with the testing of several new devices. The devices evaluated to date are summarized in Table 9. New testing focussed on developing four

Table 9 Summary of Experimental Methods Developed for Emulsion Breakers

Method Number	Description	Vessel	Energy Input	Vessel Size (mL)	Water Amount (mL)	Mousse Amount (mL)	Energy Variation	Mixing Time (min)	End Point Analysis	Advantages	Disadvantages
1	Mockay	bottle	rotation-v	500	400	50	50 rpm	60	height	known test	no access to oil/water
2	Magnetic Stirrer	cylinder	rotation-h	500	500	10-50	50-400 rpm	60-300	height	access to o/w	unstable emulsion
3	Burrell	separatory funnel	arc	500	400	30	1-3 deg	60 var	volume	simple, easy	volume unrepeatable
4	Burrell	separatory funnel	arc	500	400	30	1-3 deg	60 var	water liberated	simple, easy	repeatability poor
5	Eberbach	bottle	reciprocating	500	400	30	none	60	water liberated	simple, easy	repeatability poor no energy variation
6	Reax	bottle	rotation-v	500	400	30	65 rpm	120	volume	simple, easy	volume unrepeatable
7	Glas-col	separatory funnel	complex reciprocation	250	200	10-50	variable	var	water liberated	simple, easy	repeatability poor
8	Burrell	separatory funnel	arc	1000	800	60	1 deg	120	viscosity	more quantifiable	slow, mechanical problems with shaker
9	Burrell	separatory funnel	arc	1000	800	85	1 deg	120	water by Karl-Fischer	more quantifiable	slow, mechanical problems with shaker
10	Burrell	separatory funnel	top-mounted arc	1000	800	85	1 deg	120	water by Karl-Fischer	more quantifiable	excess water in emulsions
11	Turbula	bottle	complex gyratory	1000	800	85	5 speeds	120	viscosity	more quantifiable	slow, lower energy
12	Turbula	bottle	complex gyratory	1000	800	85	5 speeds	120	water by Karl-Fischer	more quantifiable	excess water in emulsions
13	Open-System Crystallizing dish	crystallizing dish	magnetic stirrer	2000	1000	50	variety of rpm	120	% emulsion remaining	simplicity	emulsion drawn into vortex
14	Open-Cylinder Graduated cylinder	graduated cylinder	magnetic stirrer	2000	2000	100	variety of rpm	120	% emulsion remaining	simplicity	emulsion drawn into vortex
15	Open-System large beaker	large beaker	magnetic stirrer	18000	5000	100	variety of rpm	1440	% emulsion	high O/W	low energy
16	Open-System De-emulsification large beaker	large beaker laboratory shaker	laboratory shaker	18000	10000	10	variety of rpm	1440	% emulsion	high O/W, 1:5000	long operating time
17	Closed-System De-emulsification separatory funnel	separatory funnel	top-mounted arc	1000	800	20	5 deg	180	water by Karl-Fischer	more quantifiable	excess water in emulsions
18	Open-System Inhibition Rotary agitator	rotary agitator	rotation	2200	500	20	50 rpm	180	% water viscosity	more quantifiable	excess water in emulsions
19	Closed-System Inhibition Blender	blender	high-speed blades	1000	100	20	15500 rpm	0.5	% water viscosity	represents worst-case situation	very high energy

types of agent tests, one series for emulsion-breaking and one for inhibition of emulsion formation. Tests for each of these were developed for open and closed systems. This is necessary to properly test those agents which have water-solubility and those which do not. This also corresponds to use patterns. Open-systems tests would represent the application of emulsion breaker or inhibitor at sea. Closed-system tests represent the addition of agent to skimmers and tanks.

Development of An Open-System Emulsion-Breaking Test

This first test to be developed was that of an open-system emulsion breaker test. Procedures currently in use utilize mixing energies that generate energy by high contact with the vessel walls. For the new procedure, the emulsion should remain at the surface without wall contact, while sufficient turbulence is applied to contact the product with the emulsion and drive the breaking process. It should also have a very high ratio of water to oil, to mimic the dilution of the sea.

The first apparatus tried was a magnetic stir bar in a shallow crystallizing dish (approx. 1 litre of salt water), with a magnetic stirrer to apply the energy. Immediately upon initiating the trial, it was found that the emulsion, even though less dense than the water, was drawn into the vortex and down to make contact with the stir bar. This undesirable effect eliminated this test from further consideration.

A taller vessel - a 2-litre graduated cylinder - was then tried, to limit the vortex and keep the emulsion at the surface. However, the added height with limited surface area meant that to generate sufficient surface activity to mimic sea conditions, a very large vortex was created. The emulsion was again drawn down into the water.

Next, a glass cylinder of 30 cm diameter and 30 cm height was utilized. The larger volume was equally ineffective at creating turbulence without submersing the emulsion. The larger surface area of the glass cylinder did allow for two magnetic stirrers to be placed side-by-side and run two stir bars on opposite sides of the cylinder, about 3 cm from the wall. This created an approximately circular path for the emulsion about two-thirds the radial distance from the centre. The difficulty of vortexing was eliminated. The greatest turbulence was exhibited nearest the centres over the two stir bars, but was not very energetic. The clump of "mousse" emulsion was allowed to run overnight with a very high ratio of demulsifying agent (1:10), to see how well the new test performed. The following morning, the emulsion was observed to have a black layer of oil over the surface exposed area of the emulsion, while the remainder was unaffected, bearing the original brown coloration. Obviously, there was too little turbulence to mix the treating agent with the emulsion.

Success was achieved when the glass cylinder was mounted in a New Brunswick Scientific Controlled Environment Shaker. Five litres of water were measured into the vessel, and the rotational energy adjusted until a wave was created, without splashing or reaching the height of the vessel wall. A clump of emulsion was placed in the vessel with a 1:100 ratio of demulsifying agent, capped and left shaking overnight. The emulsion was found to travel a path in the vessel about one-half the radial distance from the centre, lagging behind the rotation of the wave, bobbing up and down through the surface of the water. The following morning, only a small fraction of the original emulsion remained. This forms the basis of the method currently in use, with a few adjustments as follows: increase the volume of water to 10 litres, increase the ratio of water to oil; adjusting the rotational energy in accord with the increased volume; expel the emulsion from a 20 cc syringe with the tip cut out to yield a 1.25 cm opening, to yield

a consistent "tube" of emulsion; adding the agent to be tested dropwise along the emulsion; and weighing the emulsion before and after the test to determine the effectiveness. An effective dosage is initially being considered to be the ratio at which 50% of the mass of the starting emulsion is lost.

Open-System Emulsion Breaker Test The shaker used is the Brunswick Scientific Controlled Environment Shaker model G-27. The test vessel is an 18-litre glass cylinder, 30 cm diameter x 30 cm height. The vessel is filled with 10 litre salt water (3.3% w/v NaCl) and 10 mL mousse formed in a blender formation (78.5 % water content). This yields an oil:water ratio of 1:5000. The oil used is a 70/30 blend of ASMB/California, API gravity of 11. The mixer is shaken at 100 rpm for 24 hours. The detailed procedures are: measure 10 litres of salt water into the 20 litre glass cylinder. Place into secured basket in the controlled environment shaker. Cut the end off a 20 cc plastic syringe to give a 1.5 cm opening. Fill the syringe with mousse. Compress to the 10 mL mark. Weigh the syringe on a microbalance. Slowly inject the mousse into the glass cylinder to yield a consistent mousse "tube". Reweigh the syringe. Add the demulsifying agent to the mousse in drops along the length of the tube. Place a square of Teflon bench protector over the glass cylinder, cap over the top with a wood cutout and secure with 75 cm tie-downs. Start the shaker 1 minute after agent application. Shake for 24 hours. Stop shaker and scoop out the remaining emulsion with a gloved hand. Care must be taken not to smear the emulsion on the glove, and to minimize picking up free water. Place the emulsion into a tared beaker and weigh the emulsion residue. Calculate the percentage of mousse lost, subtracting the value for the blank runs. Product effectiveness is considered to be the treatment ratio at which 50% of the mass of the emulsion is lost.

The first tests with this new method have been completed on two products, 60% Alcopol O solution, and Vytac DM. Similar results compared to those obtained using the previous methods, however, with the advantage of the large oil:water ratio. The test results are summarized in Table 10.

Development of A Closed-System Emulsion-Breaking Test

A test to measure the ability of products to break emulsions in situations where water is not abundant is easier to develop. The wrist-action shaker noted above was adapted for this purpose. The specific methodology is as follows:

Closed-System Emulsion-Breaking Test - The shaker is a Burrell wrist action shaker model 75 equipped with a top-platform mount with large separatory funnel clamps. The test vessels are Nalgene 1 litre Teflon separatory funnels with screw-cap lids. The fill is 800 mL salt water (3.3% w/v NaCl) and 20 mL mousse. This yields an oil:water ratio of 1:200. The emulsion is formed in a blender and has 78.5% water content. The oil is a 70/30 blend of ASMB/California, API gravity of 11.0. The shaker is operated at a 5 degree arc oscillation at 20 cm radius. The shaking time is 3 hours and 15 minutes settling time is allowed before analysis. The detailed procedures are: measure 800 mL salt water into the separatory funnel. Place the separatory funnel on the balance. Measure 19.9 g (20 mL) mousse into the funnel. Using a micropipette, add appropriate volume of demulsifying agent, applying the agent directly to the surface of the mousse. Cap the funnels and insert into the clamps on the top platform; be sure all apparatus are at 90 degree angles. Move adjustment arm on the Burrell shaker until an arc of 9 degrees is obtained. Shake for 3 hours. Remove from the shaker and allow emulsion residue to settle for 15 minutes. Drain the water and pour/scoop the emulsion into an appropriately sized beaker. Wipe sides with a rubber policeman to get remaining emulsion. Measure the water content. Product effectiveness is considered to be the ratio at which 10% of the water content is lost.

Table 10 Emulsion-Breaking Test Results - Open System

ALCOPOL				
Weight		Change	Volume	Ratio
Initial	Final	%	Product	D/O
g	g		(μ L)	
8.7100	0	100.0	200	10
8.9295	0	100.0	200	10
8.8852	1.3453	83.5	100	20
8.6271	3.1866	59.8	40	50
8.8424	4.0634	49.9	40	50
8.6024	6.7954	13.9	20	100
9.0812	7.0717	16.0	20	100
8.8811	7.1660	12.9	4.0	500
9.1117	7.3364	12.3	4.0	500
8.6620	7.1284	11.2	2.0	1000
8.4935	7.6808	1.5	0.2	10000

VYTAC DM				
Weight		Change	Volume	Ratio
Initial	Final	%	Product	D/O
g	g		(μ L)	
8.9122	0	100.0	200	10
9.0404	2.0918	75.0	200	10
8.8974	2.7182	66.7	40	50
8.6977	2.1618	73.2	40	50
9.0084	3.7292	55.3	20	100
8.9063	3.9832	51.3	20	100
8.8044	6.1973	23.3	4.0	500
8.6316	5.4673	31.6	4.0	500
8.4546	6.0635	22.6	2.0	1000
8.9538	7.8126	5.0	0.2	10000

Reference Blanks		
Weight (g)		Change
Initial	Final	%
8.4105	7.6613	8.9
8.3113	7.6936	7.4
9.1068	8.5233	6.4
8.9713	8.2278	8.3
average		7.8
		Value of Blank

Test results using the products, Vytac DM and Alcopol, are shown in Table 11.

Inhibitor Tests

The procedures for the formation of emulsions can also be used for the testing of product's ability to inhibit the emulsification. The two formation procedures chosen were the two best able to form stable emulsions: the blender and the rotary agitator. For these tests, the formation procedure is followed, with the exception that an emulsion inhibitor is added to the oil in the vessel before mixing energy is applied.

Two products have been tested for their ability to inhibit emulsions, 60% Alcopol O solution and Vytac DM. Both have been tested for their ability to break emulsions. A comparison of the results for the two products is similar to their emulsion breaking results. The Vytac DM product was effective at a lower treatment ratio, giving a black product of much lower viscosity. On the other hand, the Alcopol product took a higher treatment ratio to be effective, but there is a sharp reduction in water content and viscosity.

A comparison of the two methods shows that both provide similar results. An interesting observation is that the blender is able to produce a seemingly-stable brown mousse at certain treatment ratios with the Alcopol product added. Some of these treated mousses then broke overnight into oil and water. It seems the high energy of the blender temporarily forms a stable emulsion, but in time, the emulsion breaker/inhibitor breaks down the emulsion. Conversely, the Vytac product was able to inhibit at the time of formation, as none of the mousses formed from treated oil turned to black oil with time. In this respect, the blender is a more rigorous test, albeit perhaps a bit high in energy to represent sea agitation.

Results from testing inhibition using the rotary agitator are presented in Table 12 and those using the blender in Table 13. Results of all the agent tests are presented in Figures 2 to 5. The lines and curves on these graphs are fit using a regression package. The regression coefficient (r^2) was over 0.8 in all cases. These figures show that the tests can yield clear values of effectiveness for the treating agents. There always exists a clear gap between the viscosity of the emulsion and the viscosity of broken emulsion. This also illustrates the utility of viscosity as a measure over that of water content, which has a tendency to be noisier.

Four tests have been developed to examine emulsion breakers and inhibitors. Table 14 below gives a summary of the values. These tests are designed to test both inhibition and breaking action in open (where water is plentiful) systems to represent application at sea and in closed systems, to represent the use of the product in a skimmer or storage vessel.

Table 11 Emulsion-Breaking Test Results - Closed System

O:W Ratio 1:water	% Water Content		Water Loss %	
	Vytac DM	Alcopol	Vytac DM	Alcopol
100	46.3	5.0	39.8	93.6
	30.0	11.0	61.1	85.7
200	48.3	17.1	37.3	77.8
	54.0	18.8	29.9	75.6
320	58.7	52.4	23.8	31.9
	49.1	44.5	36.3	42.2
400	56.4		26.7	
500	60.2	51.9	21.8	32.6
	59.9	66.8	22.3	13.2
625	64.7	61.1	16.0	20.7
		69.5		9.8
800		65.7		14.7
		74.2		3.7
1000	64.5	71.7	16.2	7.0
	67.8	71.0	12.0	7.8
1250	64.8		15.8	
	64.6		16.1	
2000	71.6	74.7	7.0	3.0
	73.8	73.8	4.2	4.2
5000	74.7	76.1	3.1	1.2
	72.7	74.9	5.6	2.8
10000	76.4	74.5	0.7	3.3
	76.3	76.8	0.9	0.3

Table 12 Inhibition Studies in the Rotary Agitator

Vytac DM

DOR ¹	Viscosity		Water Content %	
	D=1 ² cP	D=5 cP		
10,000	471200	113710	84.7	Lt. Brown
8000	477900	116100	85.2	Lt. Brown
6000	421600	109500	84.7	Dk. Brown
5000	369200	99160	83.9	Dk. Brown
4000	242500	75840	81.6	Dk. Brown
2000	135300	45810	81.4	Black
1000	37690	13990	71.8	Rag
100	14770	6086	74.1	Rag

Alcopol

DOR ¹	Viscosity		Water Content %	
	D=1 ² cP	D=5 cP		
10,000	439000	108200	84.6	Lt. Brown
8000	446600	115000	85.3	Lt. Brown
6000	131500	44170	81.0	Dk. Brown
4000	119800	40590	80.4	Dk. Brown
2000	96630	35200	79.7	Dk. Brown
1000	2980	2354	52.2	Rag
100	-	-	8.2	Oil

1 - De-emulsifier-to-Oil Ratio

2 - shear rate in reciprocal seconds

Table 13 Inhibition Tests in The Blender

Vytac DM

DOR ¹	Viscosity		Water Content %	
	D=1 ² cP	D=5 ² cP		
Blank	203200	50000	74.9	Brown
10,000	114000	36950	74.5	Brown
4000	109700	31050	76.9	Brown
3000	93140	25280	75.8	Brown
2000	9356	3267	76.7	Black
1500	7042	2903	78.0	Black
1000	3096	1941	49.1	*Black
400	2234	1419	44.3	2 phase
100	1277	784	18.6	2 phase

*Note - Forms a black emulsion, then breaks into two phases.

Alcopol

DOR ¹	Viscosity		Water Content %	
	D=1 ² cP *	D=5 ² cP		
Blank	203200	50000	74.9	Brown
10,000	208600	42680	69.4	Brown
2000	206600	45470	76.1	Brown
1000	106900	30810	71.9	*Brown
800	2095	1290	60.1	**Brown
600	570	388	9.0	**Brown
500	576	432	8.3	2 phase
100	-	-	2.9	2 phase

*Note - Forms a brown mousse, then 1/4 breaks into 2 phases.

**Note - Forms a brown mousse, then breaks to 2 phases overnight.

1 - De-emulsifier-to-Oil Ratio

2 - shear rate in reciprocal seconds

Table 14 Summary Results of Emulsion Breaking and Inhibiting Tests

Action	System	O:W Ratio	Shaker/Device	Results (min. operative dose)
Breaking	Open	1:5000	New Brunswick	Vytac 1:300 Alcopol 1:200
	Closed	1:200	Burrell	Vytac 1:250 Alcopol 1:280
Inhibition	Open	1:25	Rotary	Vytac 1:6000 Alcopol 1:2000
	Closed	1:4	Blender	Vytac 1:7000 Alcopol 1:2500

Figure 2

Test Results - Emulsion Breaking - Open System

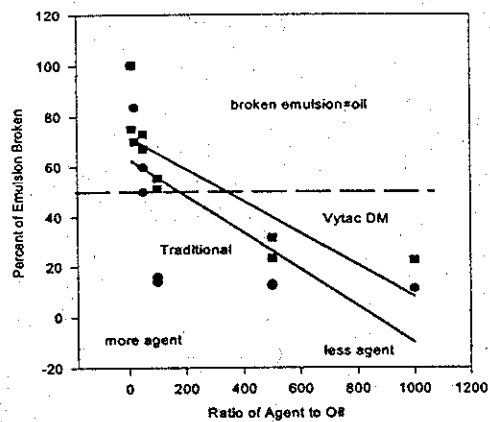


Figure 3 Test Results - Emulsion Breaking Closed System

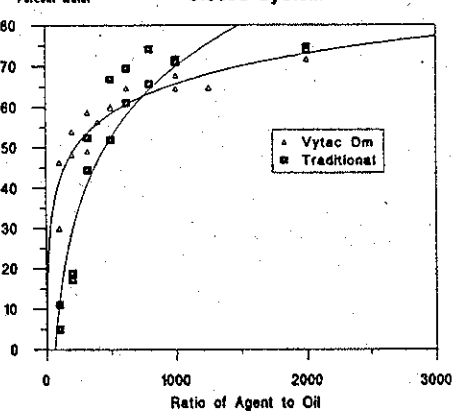


Figure 4

Test Results - Inhibition - Open System

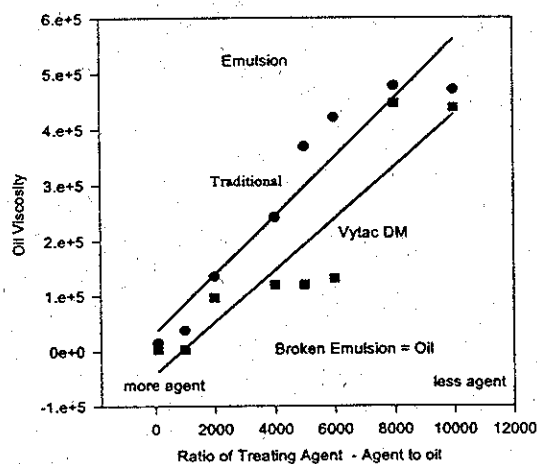
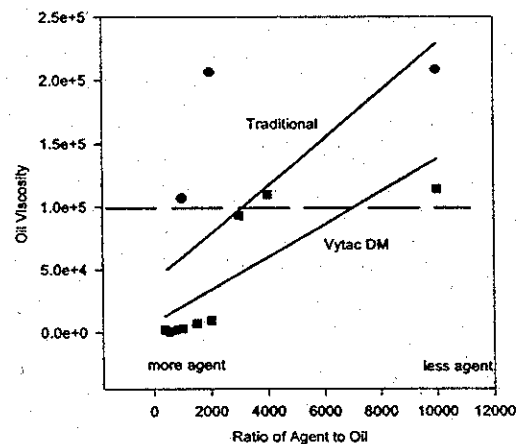


Figure 5

Test Results - Inhibition - Closed System



Emulsion Breaking in The Absence of Water

There have been questions raised about the effectiveness of the Vytac DM product to break emulsions without a water medium present. To answer these questions, a method was developed to provide agitation of the emulsion similar to the effectiveness tests in use, but without the water medium. The emulsion must be sufficiently plentiful within the mixing vessel to avoid loss to the walls. Too little emulsion will merely smear on the walls and remain. To accommodate the smaller volume of emulsion, an adaptation of the Turbula test was used. In the test, 50 mL of emulsion were placed in two 125-mL Nalgene bottles fit end-to-end in the basket of the Turbula and mixed for 3 hours. A varying amount of Vytac DM was added. From the data shown in Table 15, it can be seen that the product is indeed effective, first reducing the viscosity, then the water content of the emulsion. Upon sitting overnight, the emulsion was further reduced for treatment ratios of 1:15, product:oil, and higher. The greatest effect was seen at the 1:12 and 1:15 ratios, then began to decrease as the dosage was increased. This is similar to the effect seen for other emulsion breaking tests, in which more product does not generate increased effectiveness beyond a certain ratio. The specific method used is as follows:

Emulsion breaking with no free water present - The mixing device is the Turbula T2C Shaker/Mixer. The mixing vessel is a Nalgene 125 mL HDPE wide mouth bottle. The fill consists of 50 mL emulsion derived from a blender formation, 78.5 % water content. The oil used to form the emulsion is a 70/30 blend of ASMB and California API=11.0. The shaker was operated at 90 rpm for 3 hours. The specific methodology is as follows: place a 125 mL bottle on a balance. Weigh in 49.7 g (50 mL) mousse. Add required amount of demulsifier by micropipette, to achieve desired ratio of agent to oil. Cap bottle and wrap in sorbent pads to fill the Turbula basket. Insert and secure with clamp rings. Two may be run simultaneously by placing bottles end-to-end in the core of the sorbent wrapping. Move drive belt to highest gear ratio. Shake for 3 hours. Remove bottles and empty contents into 100 mL beaker using a rubber policeman. Analyze sample for water content and viscosity.

Summary and Conclusions

Investigations in the analytical means for characterizing emulsions shows that the measurement of water in emulsion using Karl-Fischer titration is accurate and rapid. This method, however, is limited by the characteristic of emulsions to contain a significant amount of "excess" water. This water is not part of the emulsion and generally consists of large water droplets accidentally trapped by the viscous emulsion. Incorporation of such water depends to a great degree on the method of emulsion formation. Methods to remove this water have been investigated. These include use of sorbents and centrifugation. Both have limitations that suggest these will not have potential for further development.

Viscosity has been found to be a very reliable method of characterizing emulsions. Viscosity measurements are somewhat subject to errors resulting from the incorporation of "excess" water, however, not to the degree that direct water analysis is. This laboratory is currently investigating the use of plate-plate devices which may have significant advantages over conventional cup and spindle devices for study emulsions. Disadvantages of this form of analysis are certainly the cost of the instrumentation (\$50,000 to \$100,000) and the larger amounts of sample required (1-20 mL, depending on device).

Conductivity was investigated as a technique to study emulsions. The findings are that stable emulsions show little difference in conductivity from unstable emulsions.

Table 15
Emulsion Breaking
In The Absence of Water

DOR ¹	Water Content %	Viscosity D=5 ² cP
1 to 1	63.6	4753
1 to 2	*57.9 68.4	4853
1 to 5	*59.6 63.7	3900
1 to 10	49.9	3072
1 to 12	*23.6 77.0	208.2
1 to 15	*27.8 77.2	186.5
1 to 20	77.7	7680
1 to 50	78.3	13190
1 to 100	78.6	14660
1 to 200	78.5	4506
1 to 500	78.5	12340
1 to 1000	78.5	9405
1 to 5000	78.5	40610

* Measured the following morning.

1 - De-emulsifier-to-Oil Ratio

2 - shear rate in reciprocal seconds

The question of emulsion stability has been re-examined. Emulsions formed in three apparatuses were examined. For laboratory purposes an emulsion is generally defined as being stable if it retains most of its water over a 5-day period and shows little reappearance of starting oil. Based on tests and previous experience in the laboratory, visual criteria have been developed to gauge whether an emulsion is stable or not. The first criteria is that of colour. A stable emulsion is almost always red or reddish in colour. Over several years of experience, only a few cases have been observed where an emulsion is red and it broke upon sitting. Only a few "black" emulsions have been made that might have been stable. These exceptions are very minority cases. The second criteria is that of water loss. Unstable emulsions will lose water and this will be visually apparent within the first day of formation. Third, unstable emulsions will break down producing "black" oil on their surface. Stable emulsions will change little in appearance.

Viscosity, water content and appearance were recorded for a series of emulsions over periods of up to 14 days. It was found that most emulsions increased in viscosity over the time period. This also correlates to the stability. It is noted that all stable emulsions increased in viscosity over the time period and that this viscosity increase could be noted in as little as 2 days and very reliably in 5 days. Those emulsions that did not increase in viscosity, are suspected to be unstable. Furthermore, these same suspect emulsions had low viscosities in comparison to the stable emulsions. These tests appear to show that stable emulsions require a viscosity of at least two orders-of-magnitude greater than the starting oil. The water content could change for the emulsions during the time period, however, this did not correlate with stability nor viscosity. A rule of thumb, which certainly requires further investigation, is that a stable emulsion is one which has a viscosity at least 10 times its starting oil viscosity and this viscosity should increase upon sitting over a 5-day period. An interesting point to note is that the emulsions produced in this test using very different energy levels were nearly an order-of-magnitude apart in viscosity. The highest energy device produces the most stable emulsion and one with the highest viscosity. Another point of interest is that the stable emulsions increased in viscosity during the 14-day period and appeared to actually become more stable.

Laboratory formation techniques were examined in 4 apparatuses. Again, it was noted that the most viscous and stable emulsions were produced in the highest energy devices. The most energetic device, a commercial blender, could produce stable emulsions from oils that a rotating flask device could not. A commercial rotary agitator shows promise for a standard formation technique at lower energy. A wrist action shaker was also tested, but the lower energy and lack of repeatability does not warrant further testing on this device. This laboratory has tested other devices in the past, however, these are not being tested further.

Four tests have been developed to assess commercial emulsion breakers and inhibitor products. The tests mimic open and closed systems and focus on emulsion breaking or inhibition of formation. The open system test for emulsion breaking employs a moving-platform shaker over a 24-hour period. The closed system employs a wrist-action shaker over a 3-hour period. The open system for emulsion inhibition uses a rotary agitator over 3 hours. The closed system employs a blender operated at pulses of 30 seconds. Two treating agents, Vytac DM and 60% Alcopol 0, were tested in these systems and found to be effective at ratios varying from 1:7000 to 1:250, depending on product and test.

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